Conference Paper

GaNPAs Solar Cells that Can Be Lattice-Matched to Silicon

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National Renewable Energy Laboratory
Golden, CO 80401

ABSTRACT

III-V semiconductors grown on silicon substrates are very attractive for lower-cost, high-efficiency multijunction solar cells, but lattice-mismatched alloys that result in high dislocation densities have been unable to achieve satisfactory performance. $GaN_xP_{1-x-y}As_y$ is a direct-gap III-V alloy that can be grown lattice-matched to Si when $y = 4.7x - 0.1$. We have proposed the use of lattice-matched GaNPAs on silicon for high-efficiency multijunction solar cells. We have grown $GaN_xP_{1-x-y}As_y$ on GaP (with a similar lattice constant to silicon) by metal-organic chemical vapor phase epitaxy with direct bandgaps in the range of 1.5 to 2.0 eV. We have demonstrated the performance of single-junction $GaN_xP_{1-x-y}As_y$ solar cells grown on GaP substrates and shown improvements in material quality by reducing carbon and hydrogen impurities through optimization of growth conditions. We have achieved quantum efficiencies (QE) in these cells as high as 60% and PL lifetimes as high as 3.0 ns.

1. Introduction

State-of-the-art GaInP/GaAs/Ge and many proposed future generations of III-V high-efficiency solar cells are based on GaAs or Ge substrates [2]. In particular, much attention has been given to GaInNAs materials grown lattice-matched on GaAs over the past few years [3]. More recently, GaNP materials have been shown to become direct gap, with only a few percent N [4]. GaNPAs alloys have been grown lattice-matched to Si [5] with band gaps that could be useful for solar cells. Growth on silicon substrates is very exciting because it would allow for significant cost savings of substrates and the potential for integration with existing Si technology. Lattice-mismatched III-V cells on Si substrates have been studied extensively, but the reduction of defect densities remains a significant challenge that typically requires complex graded buffer layers. We have proposed a structure based on lattice-matched $GaN_xP_{1-x-y}As_y$, hereafter GaNPAs, alloys grown on silicon [6,7]. The solar cell structure shown in Fig. 1, composed of a lattice-matched III-V cell grown on a Si cell, could potentially rival the efficiencies of high-efficiency cells on GaAs or Ge,

1.7 eV GaNPAs junction
tunnel junction
1.1 eV Silicon junction (silicon substrate)

Fig. 1. Proposed lattice-matched GaNPAs on silicon tandem solar cell.

with significant cost savings and improvements in mechanical stability. Indeed, a two-junction cell composed of a 1.65-eV to 1.75-eV GaNPAs junction on a 1.1-eV silicon junction has a nearly optimal set of band gaps for high-efficiency solar cells, as shown in Fig. 2.
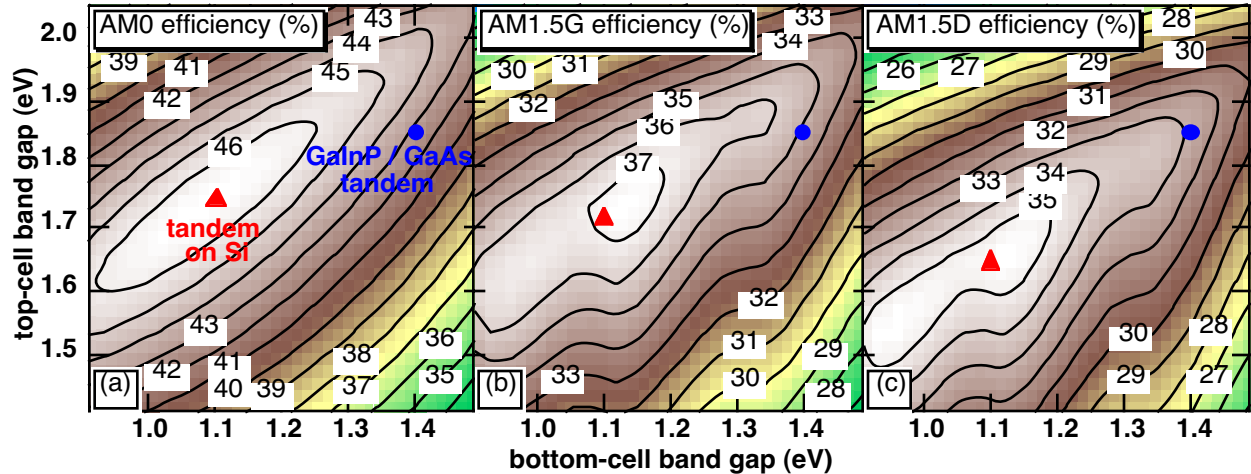
Fig. 2. Iso-efficiency contour plots of ideal series-connected, two-junction solar cell with an optimized top cell thickness [1], as a function of top-cell and bottom-cell direct band gap using standard spectra: (a) AM0 (space), (b) AM1.5 global (terrestrial), (c) AM1.5 direct (concentrator terrestrial). All efficiencies were calculated at 300 K and 1–sun conditions. The red triangles show optimal GaNPAs/Si tandems, and the blue circles show the standard GaInP/GaAs tandem cell.

GaP is only 0.36% lattice-mismatched with silicon, and growth on GaP substrates avoids some of the difficulties associated with growth on silicon. Therefore, as a first step, we have studied GaNPAs solar cells grown on GaP substrates.

2. Material Properties

GaNPAs layers were grown by atmospheric-pressure metal-organic vapor-phase epitaxy (MOVPE) on (001)-oriented, double-side-polished GaP wafers using trimethylgallium (TMG) or triethylgallium (TEG), unsymmetric-dimethylhydrazine (DMH), phosphine (PH_3), and t-butylarsine as sources. Growth was performed at 600°–700ºC, with nominal growth rates (GR) of 2–4 μm/h, and PH_3/Ga ratios of 6–52. Incorporation efficiencies of the group-V elements follow the trend of As>P>N and are highly temperature dependent. Whereas N incorporation drops off with increasing temperature, P incorporation increases relative to As. Thus, achieving the intended compositions required a sensitive balance between group-V source flows and temperature. By carefully adjusting the group-V flows, alloys nearly lattice-matched to GaP were grown.

A series of GaNPAs layers were grown directly on double-side-polished, undoped GaP substrates to determine the absorption coefficient (α). Simultaneous reflectance (R) and transmittance (T) measurements of the layer were used to determine $\alpha(\lambda)$ below the band gap energy of the GaP substrate, and spectral ellipsometry (SE) measurements were used above the band gap of the substrate. Fig. 3 shows the absorption for several different compositions of GaNPAs. The strong direct-like absorption in this spectral range indicates that these alloys may be quite useful as solar cell absorber layers. The absorption edge indicated band gaps in the range of 1.5 to 2.0 eV for different compositions lattice-matched to GaP.

Double-crystal x-ray diffraction (DCXRD) was performed in the (004) reflection and, in some cases, (115) reflections. Nitrogen composition in GaNP was estimated using Vegard's law. Fig. 4 shows how closely the GaNPAs
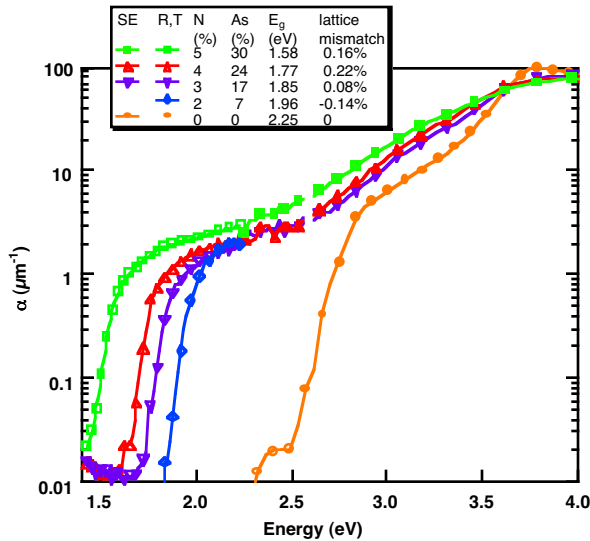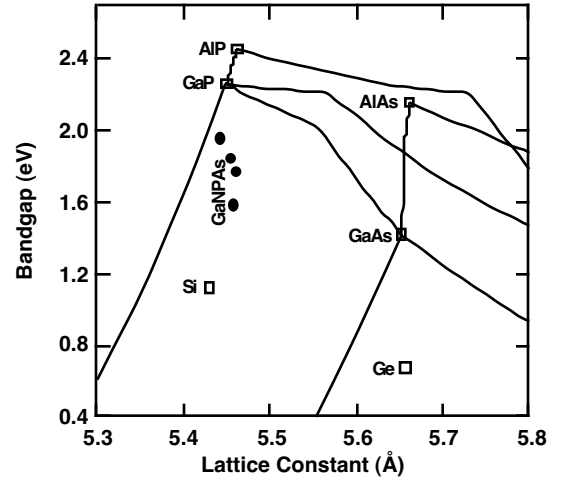

Fig. 4. Band gap vs. lattice constant of III-V semiconductors including data for GaNPAs alloys from Fig. 3.

layers were lattice-matched to GaP and Si.

We have also studied the incorporation of carbon and hydrogen impurities into GaNP grown by MOCVD and have shown how growth temperature, growth rate, gallium source, and group V fluxes strongly influence the incorporation of these impurities [8]. Impurity concentrations of carbon in similar compositions of GaNP can vary from the secondary-ion mass spectrometry (SIMS) detection limit (about 1×10^{17} cm^{-3}) to about 1×10^{20} cm^{-3}, depending on growth conditions. The behavior of carbon incorporation depends strongly on whether the dominant carbon source is the gallium source or the nitrogen source. When DMH dominates as the carbon source, similar carbon concentrations result using either TEG or TMG. These conditions result when high flow rates of DMH are used to achieve sufficient nitrogen incorporation at higher temperatures (>700°C). When the gallium source dominates as the carbon source, similar carbon concentrations result, whether growing GaP without DMH or GaNP with DMH; but much greater carbon incorporation occurs using TMG rather than TEG. The carbon incorporation when the gallium source dominates drops dramatically with increasing growth temperature. To minimize the carbon incorporation in a given composition of GaNP, an optimal growth temperature exists (650°–700°C for $GaN_{0.02}P_{0.98}$), that balances the two mechanisms of carbon incorporation. The effects of the group-V fluxes on the carbon incorporation also depend on which mechanism of carbon incorporation dominates.

The hydrogen and carbon incorporation in GaNP are strongly correlated even when it is intentionally doped with carbon only (see Fig. 5). Measurements of the photoluminescence (PL) decay lifetime [8] show that the electrical quality of the material is also correlated with the carbon and hydrogen concentration, implying that carbon and/or hydrogen form a deep-level complex that is detrimental to the electrical quality of GaNP. Fig. 5 shows the codependence of PL lifetime, hydrogen, and carbon concentration. Lifetimes as long as 3 ns were achieved in the samples with the lowest concentrations of carbon and hydrogen. It should be noted that these lifetimes were achieved for samples with no surface passivation and large lattice-mismatch. Understanding the effects of growth conditions on impurity concen-

SE	R,T	N (%)	As (%)	E_g (eV)	lattice mismatch
■	■	5	30	1.58	0.16%
▲	▲	4	24	1.77	0.22%
▼	▼	3	17	1.85	0.08%
●	●	2	7	1.96	-0.14%
○	○	0	0	2.25	0

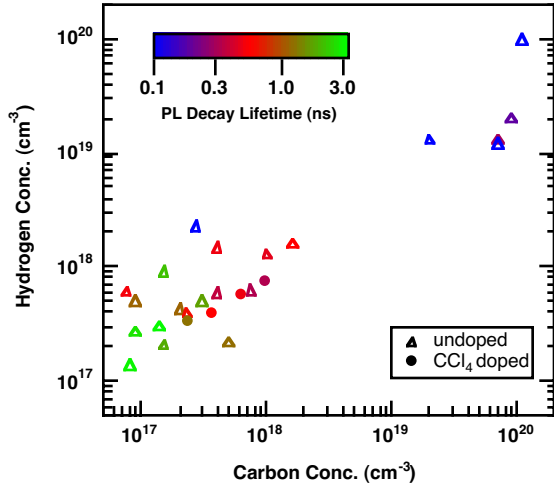Fig. 3. Absorption coefficient of $GaN_xP_{1-x-y}As_y$ layers grown on GaP substrates. The GaP substrate is shown as circles.

Fig. 5. PL decay lifetime of $GaN_{0.02}P_{0.98}$ (indicated by color) as a function of carbon and hydrogen concentration (determined by SIMS).

ured to calculate the internal QE. The internal QE is shown in Fig. 7a for three solar cells grown at different growth rates. The integrated current was calculated from the AM1.5 global spectrum and used to set the light level on an XT-10 solar simulator. The current-voltage (IV) curves were measured both in the light and dark. The IV curves corresponding to the cells from Fig. 7a are shown in Fig. 7b.

Fig. 6. Single-junction GaNPAs cell structure.

The carrier concentration in the nominally undoped GaNPAs base and similar layers was measured by capacitance-voltage (CV) measurements. The layers were found to be p-type (on the order of $1x10^{16}$ cm^{-3}) under white light bias, but were depleted when measured in the dark (see Fig. 7c).

The impurity carbon and hydrogen concentrations of GaNPAs material grown under the same conditions as these cells were measured by SIMS. These results are summarized in the legend of Fig. 7a. These impurity levels changed significantly by changing only the growth rate. In all cases, the carbon concentration was greater than the carrier concentration measured by CV in the light. This indicates that carbon is not acting only as a shallow dopant. The QE and J_{sc}, on the other hand, correlate strongly with the carbon and hydrogen concentrations. This is further evidence that carbon and/or hydrogen form a deep-level complex that is detrimental to the diffusion length.

Another interesting effect in these GaNPAs cells can be observed in the dark IV curves of Fig. 7b. The dark IV curve of the cell grown at 4 μm/h has a much higher turn-on voltage than its corresponding light IV curve. This effect is typical of the GaNPAs cells discussed previously [7]. It
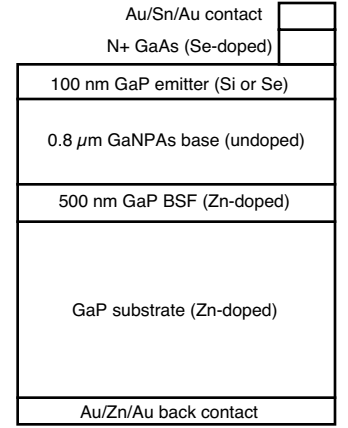
trations in GaNP is thus essential to improving device properties of GaNPAs solar cells.

3. Solar Cells

We have studied GaNPAs solar cells with direct bandgaps ranging from 1.6–1.9 eV [7]. We have grown and measured cells using the simple single heterojunction cell design shown in Fig. 6. The cells consisted of a Zn-doped GaP back surface field, an undoped GaNPAs base, a Si-doped GaP emitter, and a Se-doped GaAs contact layer. The cells were grown on Zn-doped (001) GaP substrates. The active GaNPAs base was grown at 650°C with TEG for minimal carbon and hydrogen incorporation. Au/Zn/Au back-side contacts and Au/Sn/Au front-side contacts were deposited and annealed at 450°C. Devices were isolated with a $KMnO_4/HF/H_2O$ mesa etch. The GaAs contact layer was selectively etched with a solution of $NH_4OH/H_2O_2/H_2O$.

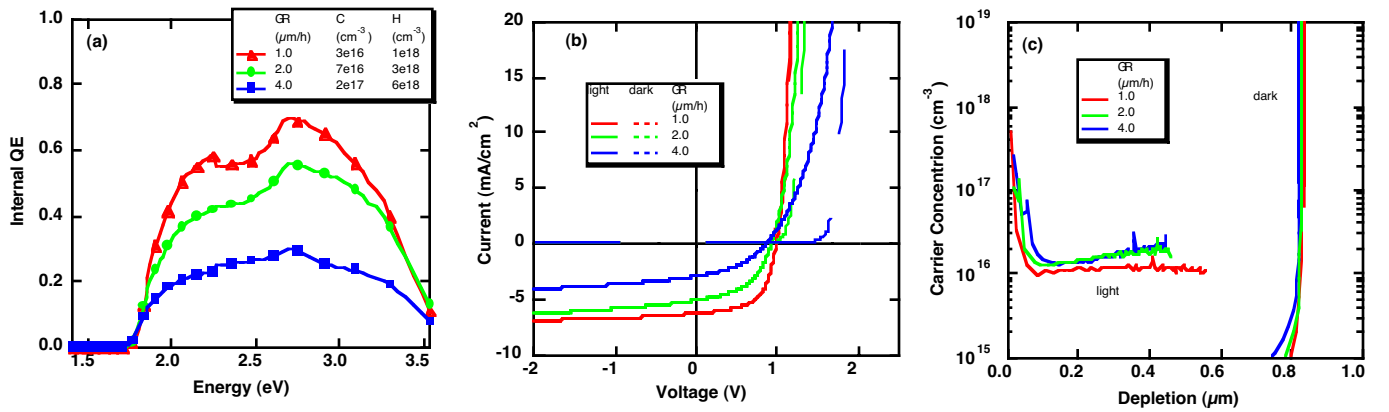The external QE and reflectance of the cells were meas-

Fig. 7. (a) Internal quantum efficiency, (b) current-voltage curves, and (c) carrier concentration profiles from CV of three GaNPAs solar cells nearly lattice-matched to GaP grown at different growth rates. Carbon and hydrogen concentrations determined by SIMS are shown in the legend. The GaNPAs layers were all grown at 650°C with identical N, P, and As source flow rates.

may be a result of the different carrier properties in the light and dark, or an unintentional pn junction within the cell structure. By reducing the carbon and hydrogen impurity concentrations (by reducing the growth rate in this case), we have managed to reduce or eliminate this effect. In addition, the fill factor is greatly improved by reducing the impurity concentrations.

A comparison of GaNPAs cells with GaInP cells that have a comparable bandgap shows that there is considerable room for improvement of the GaNPAs cells [7]. The reduction of carbon and hydrogen impurity concentrations by better understanding the effects of growth conditions has allowed us to significantly improve the properties of GaN-PAs solar cells, but further improvements in the electrical properties of GaNPAs are necessary to realize the high-efficiency tandem solar cell on silicon considered here. Future work will also focus on the growth of lattice-matched GaNPAs on silicon substrates. The growth of lattice-matched GaNPAs on silicon is challenging due to the polarity and thermal expansion mismatch between III-V and silicon. Fortunately, these problems seem to have been solved to some extent [5].

4. Conclusion

Lattice-matched GaNPAs solar cells on GaP substrates have been demonstrated with absorption characteristics appropriate for the top cell of an optimal lattice-matched III-V on silicon tandem solar cell. The performance of these cells was less than ideal, suggesting problems with the electrical quality of this novel material. Improvements in solar cell performance and PL lifetimes have been achieved by reducing carbon and hydrogen impurity concentrations through optimization of growth conditions. We have achieved QE in these cells as high as 60% and PL lifetimes as high as 3.0 ns.

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